



Visible light responses of sulfur-doped rutile titanium dioxide photocatalysts fabricated by anodic oxidation

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ARTICLE INFO

Article history:

Received 6 February 2009

Received in revised form 11 May 2009

Accepted 13 May 2009

Available online 20 May 2009

Keywords:

Sulfur doping

Titanium dioxide

Rutile

Anodic oxidation

Visible light response

ABSTRACT

Anodic oxides on pure titanium provide rutile-structured TiO₂ photocatalysts with sub-micron pores. The photocatalysts effectively bleached methylene blue aqueous solution under visible light illumination with wavelengths longer than 413 nm. Auger electron spectroscopy and infrared absorption analyses revealed the presence of sulfur in the anodized oxide. The sulfur doping appears to play an important role in response to visible light by narrowing the band gap of pristine TiO₂.

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1. Introduction

TiO₂ is regarded as one of the most useful photocatalysts due to its broad functionality, long-term stability and non-toxicity, since its properties were first reported by Honda and Fujishima [1]. A number of methods have been employed to fabricate the TiO₂ such as sol–gel methods [2], thermal chemical vapor deposition [3], thermal spraying [4], and sputtering [5], along with anodic [6] and thermal oxidation [7]. The authors have employed anodic oxidation to immobilize TiO₂ on the surface of titanium and its alloys [8]. It has been demonstrated that the rutile-structured TiO₂, when prepared in the high concentration sulfuric acid electrolyte, exhibits higher activities in bleaching methylene blue (MB) than the anatase TiO₂ [9] and better superhydrophilicity as compared with anatase [10].

TiO₂ is a semiconductor with a wide band gap (anatase, 3.2 eV; rutile, 3.0 eV) and acts as a photocatalyst only under UV light. However natural solar light contains only a few percent of its total energy in this region. In order to activate the photocatalysts to visible light, it is necessary to change the electronic structure to give a band gap which corresponds to visible light. Doping is an effective method of modifying the electronic structure of TiO₂, and metal doping has been extensively reported [11–13]. Systematic

studies on the doping of single-crystalline TiO₂ by an ion-implantation method was first reported by Koshida and Yabumoto, who found that Na⁺ and Li⁺ implanted TiO₂ that exhibited an enhancement in the absorption of visible light [14]. Similar studies by Anpo and Takeuchi [15] reported that the photocatalytic activity for NO decomposition of the implanted photocatalysts was several times higher than that of monolithic TiO₂ under outdoor solar illumination.

On the other hand, the study by Asahi et al. triggered the investigation of anionic doping with carbon, nitrogen, fluorine and sulfur [16]. The calculations in that study used the full potential linearized augmented plane wave (FLAPW) formalism and concluded that anionic doping was more effective to suppress localization of the d states of titanium deep in the band gap of TiO₂ than cationic doping. They prepared nitrogen-doped TiO₂ photocatalysts by annealing TiO₂ under a nitrogen atmosphere and confirmed photocatalytic activity in visible light. The substitution of nitrogen atoms for oxygen sites in TiO₂ made the band gap narrower. First principle calculations and X-ray photoelectron spectroscopy (XPS) indicated this was caused by the mixing of nitrogen and oxygen 2p states. Afterward, similar studies have reached the same conclusions and the effectiveness of anion doping has been widely accepted.

Likewise, sulfur doping has been studied to bring about similar narrowing of the band gap. Ohno et al. reported that TiO₂ doped with sulfur, which had been prepared by sol–gel techniques using thiourea as the source of sulfur, exhibited photocatalytic activity

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under visible light [17,18]. They proposed that the Ti^{4+} cations were substituted by sulfur cations (S^{4+} or S^{6+}) and a new level, coming from sulfur 3p orbitals located above the valence band, narrowed the band gap. Umabayashi et al. reported that sulfur-doped TiO_2 prepared by the oxidation of TiS_2 powder [19,20] or by sulfur ion implantations [21], gave TiO_2 with sulfur atoms occupying oxygen atom sites forming Ti–S bonds. The mixing of S 3p states with the valence band reduced the band gap and resulted in visible light responses. Recently, Tang et al. reported that sulfur-doped TiO_2 could be prepared by annealing anodized titanium foils in a flow of H_2S . Sulfur ions were incorporated into the oxygen sites in TiO_2 nanotubes and formed O–Ti–S bonds [22]. These results were supported by XPS measurements showing that the non-metal doping broadens the Ti 2p peaks towards lower energies, and changes the valence band state [23]. However, there are some skepticisms on the band gap narrowing by doping [24] and the mechanisms of the visible light responses have not been delineated.

In the present study, we show visible light response of TiO_2 photocatalysts prepared by anodic oxidation in a sulfuric acid electrolyte. The anodic oxidation for titanium and its alloys allows minor element doping to the oxide by selecting the composition of the electrolytes, resultantly it enables the control of the band gap of the oxide [25]. The effects of sulfur doping by anodic oxidation on the photocatalytic activities were explored through careful analysis on sulfur.

2. Experimental methods

Titanium plates (cp-Ti, grade I, $1.0\text{ cm} \times 2.0\text{ cm} \times 0.1\text{ cm}$) were used for an anode in the anodic oxidation. They were polished using a 40 nm colloidal silica suspension followed by rinsing in ethanol using an ultrasonic cleaning bath. A constant current of 50 mA cm^{-2} was applied to the titanium plate in a sulfuric acid electrolyte (0.02, 0.1 and 1.2 M), and a Pt mesh electrode (25 cm^2) was used as the cathode. The anodic oxidation was controlled galvanostatically and the oxidation was conducted for 0.5 h. The anodized titanium was rinsed with distilled water and then dried at room temperature, followed by annealing at 723 K for 5 h in air.

The crystallographic structure of the anodized oxide was determined by X-ray diffraction (PANalytical X'Pert diffractometer, Netherlands) with Cu $K\alpha$ radiation (0.15406 nm), at a scan rate of $1^\circ/\text{min}$, and a rotating detector. The sample was set in a thin-film geometry arrangement at 0.5° glancing angle. For the XRD measurements, a multiple array detector was used, which increases the recording speed by up to 100 times without lowering the resolution of the conventional detector. Microstructure observations were conducted with a field emission scanning electron microscopy (FESEM, FEI XL-30FEG, USA) at an operating voltage of 3–15 kV. The diffusion reflection spectra were measured with a UV–vis spectrophotometer (Jasco V-550, Japan) equipped with an integration sphere.

The photocatalytic activity was evaluated by methylene blue (MB) bleaching tests. The anodized TiO_2 was placed in a disposable PMMA cell ($1\text{ cm} \times 1\text{ cm} \times 4.4\text{ cm}$) containing 2 ml of 10 mg/l MB aqueous solution. Visible or UV light from a Xe lamp (Asahi Spectra, Max-301, 300 W, Japan) was passed through a 365, 400, 440, 500, or 550 nm band pass filter. The photon fluxes of the light passing the filter were 2.13, 1.34, 2.17, 2.88 or $3.43 \times 10^{-9}\text{ E cm}^{-2}\text{ s}^{-1}$, respectively. The bandwidth of the passed light was about 10 nm. The MB bleaching test was carried out by measuring the absorbance of MB at 664 nm using a UV–vis spectrophotometer after illumination for 1, 2, 3 and 4 h. Prior to the bleaching tests, the photocatalysts were immersed in MB solutions for more than 12 h to complete the adsorption of MB molecules on the surface of the photocatalyst.

The sulfur distribution was investigated in depth with Auger Electron Spectroscopy (AES, JEOL JAMP-7100E, Japan), and Ar ion sputtering was carried out at an energy of 3 keV and the sputtering rate of 0.083 nm s^{-1} for SiO_2 .

3. Results and discussion

The anodized oxide became a lighter grey as the sulfuric acid concentration in the electrolyte increased. The FESEM observation (Fig. 1) shows the microstructures in the anodized oxides prepared in electrolyte solutions containing 0.02 M (a), 0.1 M (b), and 1.2 M (c) sulfuric acid. The micro-sized pores increased in frequency with increasing sulfuric acid concentration. Concurrently, with increasing concentration the pores coalesced into larger-sized pores and the surface roughness of the oxide increased. Distinct microcracks were not observed in the oxides regardless of the sulfuric acid concentration, probably due to the relief of internal stress by pore generation.

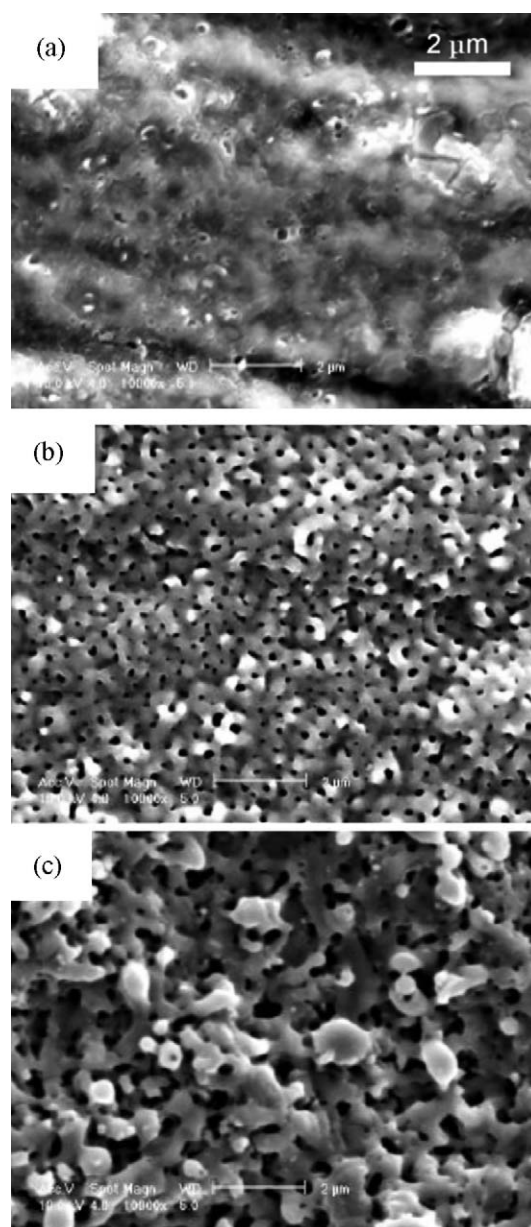


Fig. 1. FESEM images of the anodic oxides prepared in an electrolyte of sulfuric acid at a concentration of 0.02 M (a), 0.1 M (b), and 1.2 M (c).

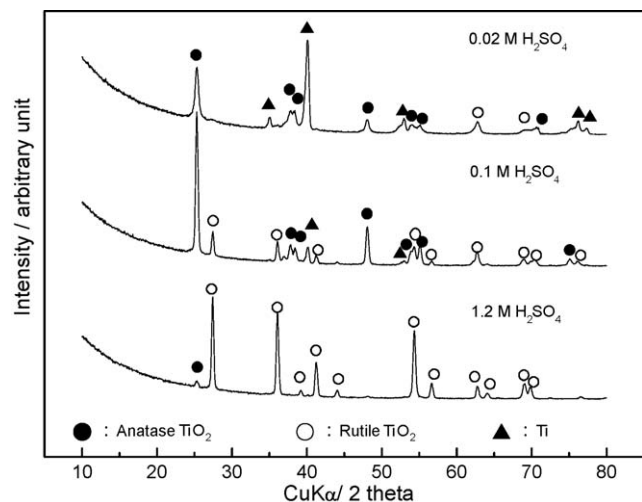


Fig. 2. XRD profiles of the anodic oxides prepared in an electrolyte of sulfuric acid at a concentration of 0.02 M (a), 0.1 M (b), and 1.2 M (c).

Fig. 2 shows the XRD profiles of the oxides prepared in an electrolyte solution containing 0.02, 0.1, and 1.2 M sulfuric acid. When the sulfuric acid concentration was low (0.02 and 0.1 M), the main peak was observed at 25.3° and has been attributed to anatase (1 0 1). The predominant phase changes from anatase to rutile at the sulfuric acid concentration of 1.2 M, wherein the main peak was observed at 27.4° and has been attributed to rutile (1 1 0) [9].

Several experimental results indicated that the photocatalytic decomposition of various dyes over illuminated TiO_2 fitted the Langmuir–Hinshelwood kinetics model [26].

$$r = \frac{dC}{dt} = \frac{kKC}{1 + KC} \quad (1)$$

where r is the degradation rate of the dye, C is the concentration of the dye, t is the illumination time, k is the reaction rate constant, and K is the adsorption coefficient of the reactant. When the initial concentration of dye is low, Eq. (1) can be simplified to an apparent first-order equation:

$$r = kKC = k_{app} C \quad (2)$$

At 10 ppm of MB solution, the relationship between $-\ln(C/C_0)$ and illumination time was linear, but not at 25 ppm MB. The apparent rate constants (k_{app}) for MB bleaching on the TiO_2 photocatalysts are presented in Fig. 3. TiO_2 anodized in 0.02 and 0.1 M sulfuric acid aqueous solution bleached MB to a certain extent when illuminated with 365 nm UV light. The rate constants of these oxides were close to that of the commercially available anatase TiO_2 . At longer wavelengths, the rate constant of the anodic oxide prepared in 0.02 M sulfuric acid aqueous solution decreased monotonously, which is similar to the commercially available anatase. In contrast, the anodic oxides prepared in 0.1 and 1.2 M sulfuric acid aqueous solution exhibited photocatalytic activity when illuminated with visible light.

The diffusion reflection spectrum of the anodized oxide prepared in 1.2 M sulfuric acid aqueous solution is displayed in Fig. 4 and shows broad absorbance across the UV–vis regions. For TiO_2 oxidized in 0.02 or 0.1 M sulfuric acid aqueous solution, the characteristic spectra could not be obtained probably because the oxide layer was too thin. Suitable diffusion reflection spectra can usually be obtained when the sample is more than $1 \mu\text{m}$ in thickness indicating the oxides prepared in 0.02 and 0.1 M sulfuric acid aqueous solution did not exceed that value.

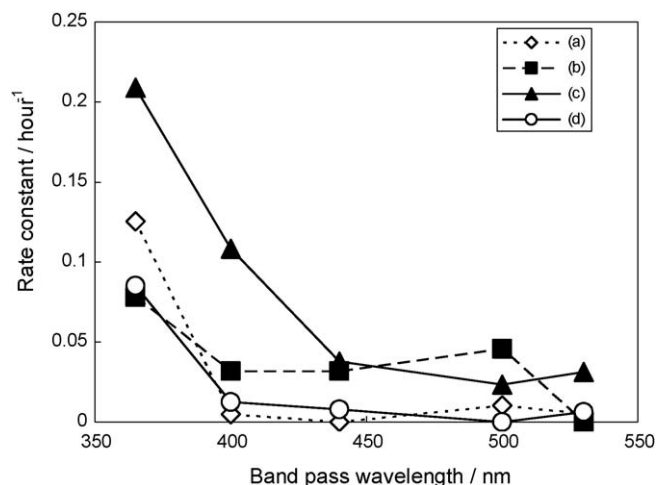


Fig. 3. Apparent rate constants for MB bleaching on the anodized TiO_2 in 0.02 M (a), 0.1 M (b), 1.2 M (c) sulfuric acid and commercially available TiO_2 (d).

Related to the influence of crystal structure on photocatalytic activities, we have considered that no intrinsic difference in photocatalytic activity exists between anatase and rutile when the decomposition reaction progresses by oxidation as MB bleaching [27]. This is because the oxidation activity depends on the energy level of the valance band and the corresponding energy level is closed to each other between anatase and rutile. From systematic investigation, we have considered that the surface area is a dominant factor affecting the photocatalytic activities of the present anodic oxides. It is generally accepted that photocatalytic reaction occurs on the surface of the photocatalyst and surface area to be absorbed by the reactants to be photocatalyzed is an important factor for the photocatalytic activities. We have measured the surface area of the anodic oxides against the sulfuric acid concentration in the electrolyte has been reported in a previous paper [9]. These results suggest that the surface area of the rutile TiO_2 is higher than that of anatase TiO_2 , which could be an appropriate explanation for the high activity of rutile TiO_2 .

Previous reports on doping TiO_2 with sulfur have employed XPS to determine the sulfur content [17–23,25]. The XPS spectra (Fig. 5) of the oxides were obtained by monochromatized Al $K\alpha$ radiation (ESCA1600, Ulvac-Phi, Japan). The S 2p peak was observed at approximately 170 eV irrespective of the sulfuric acid concentration, as shown in (a). This peak has been ascribed to the S^{4+} ion of SO_2 molecules adsorbed on a TiO_2 surface [28]. However, it is

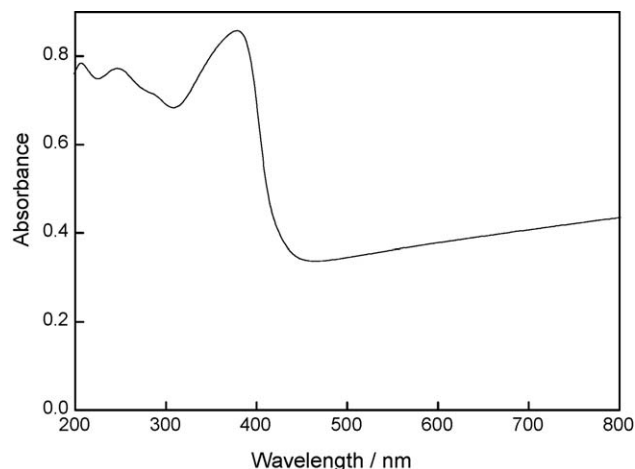


Fig. 4. Reflection diffusion spectrum of the anodic oxide prepared in an electrolyte of sulfuric acid at a concentration of 1.2 M.

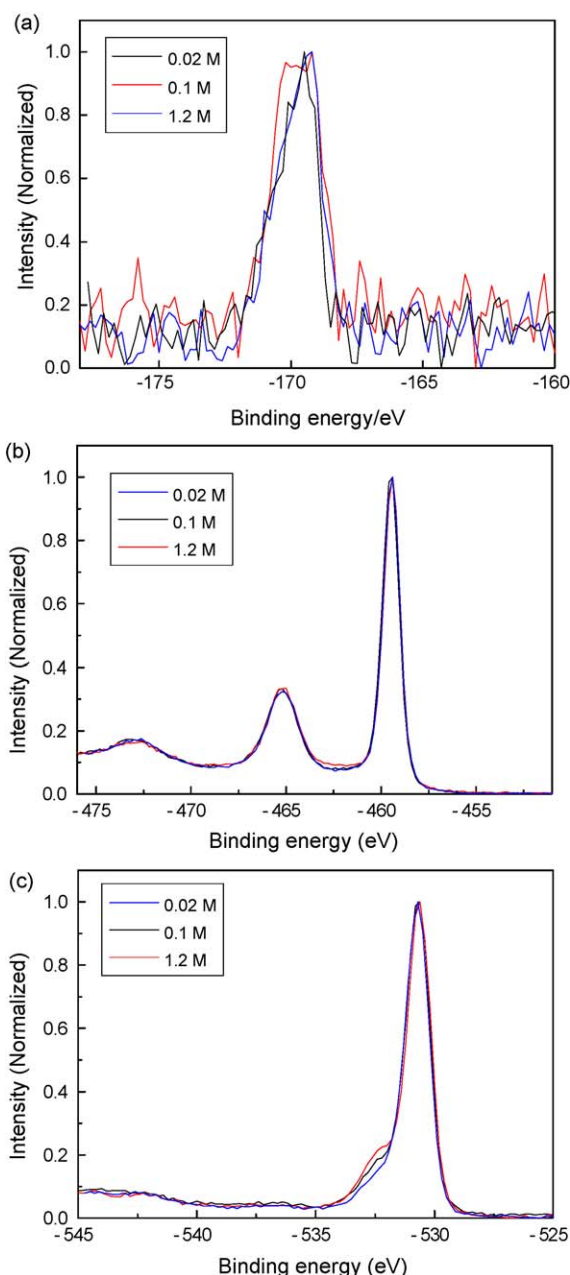


Fig. 5. (a) S 2p, (b) Ti 2p, (c) O 1s XPS spectra of the anodized TiO_2 prepared in an electrolyte of sulfuric acid at a concentration of 1.2 M.

difficult to distinguish between doped sulfur in the surface and contaminants originating from the sulfuric acid in the electrolyte due to the overlap of the binding energy. The XPS spectra of the Ti 2p and O 1s regions are shown in Fig. 5(b) and (c), respectively. The spectrum of Ti 2p XPS exhibits a symmetrical profile, irrespective of the sulfuric acid concentration, which indicates that reduced Ti^{3+} ions are not present in the anodic oxides. The shoulder peak at approximately 533 eV in the O 1s XPS was assigned to the adsorption of hydroxyl groups [29,30], and the intensity of this shoulder peak increased with increasing sulfuric acid concentration whereas the Ti 2p and S 2p peaks were independent of sulfuric acid concentration. These additional hydroxyl groups are probably responsible for the superhydrophilicity [10].

The TiO_2 prepared in 1.2 M sulfuric acid aqueous solution was subjected to AES analysis to explore the distribution of sulfur. The AES differential spectra before and after Ar sputtering for 60, 120 and 240 s show titanium, oxygen, sulfur and carbon peaks (Fig. 6(a)).

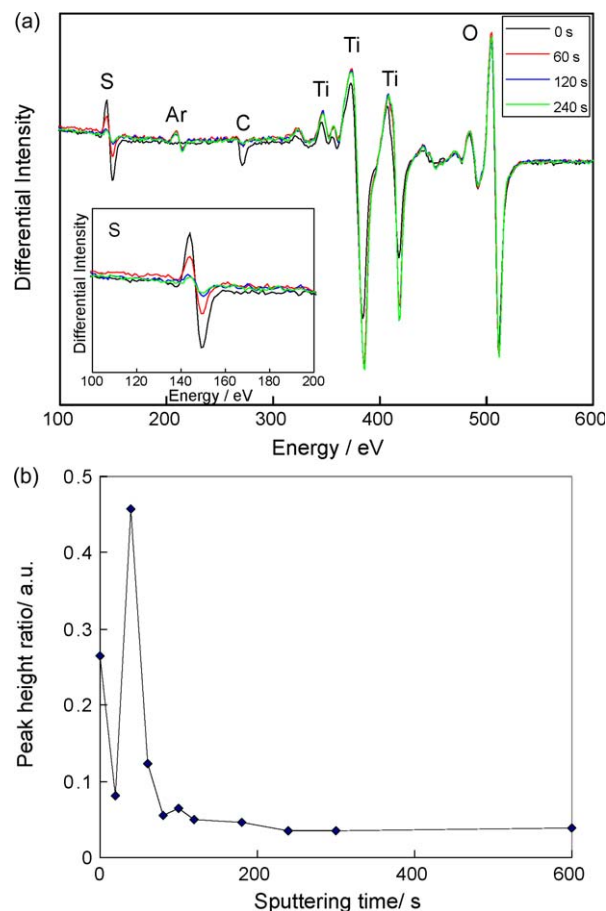


Fig. 6. (a) The wide scan of AES spectra of the oxide anodized in an electrolyte of sulfuric acid at a concentration of 1.2 M before sputtering and after sputtering for 60, 120 and 240 s, and (b) a plot of the peak height ratio of sulfur (152 eV) to titanium (418 eV) during argon sputtering.

These results suggest that sulfur has been doped into the anodic oxide. The ratios of the height of the sulfur (152 eV) to titanium (418 eV) peaks during argon ion sputtering are plotted against the sputtering time in Fig. 6(b), revealing monotonous decrease in the relative height of the peaks with increasing depth. The scattering of the peak height ratios observed in the initial sputtering time was attributed to the removal of carbon contaminants.

The amount of sulfur was determined by measuring SO_2 which had been extracted from the anodic oxide on titanium substrate during combustion in high frequency furnace, by the infrared absorption method. The amount of sulfur in the un-anodized titanium substrate, as measured by the same method, was below the detection limit of 0.3 μg , and the differences between this and sulfur contents in the anodized sample were defined as the amount of sulfur in the anodic oxide. The amount of sulfur in the anodic oxide was plotted against the sulfuric acid concentration in the electrolyte in Fig. 7. It increased monotonously with an increase in the concentration of sulfuric acid, suggesting that the amounts of doped sulfur can be controlled with the sulfuric acid concentration in the electrolyte. In the case of the TiO_2 anodized in 1.2 M sulfuric acid aqueous solution, 2 μg of sulfur was detected. Assuming that the titanium substrate was homogeneously coated with a layer of TiO_2 7 μm in thickness, as derived from the cross-section TEM observation [9], and that the density of the formed TiO_2 was the same as bulk TiO_2 , the sulfur concentration in the anodized TiO_2 layer was 110 ppm. Considering the porous microstructure of the anodic oxide, the true sulfur concentration in the anodic oxide should be more than this value.

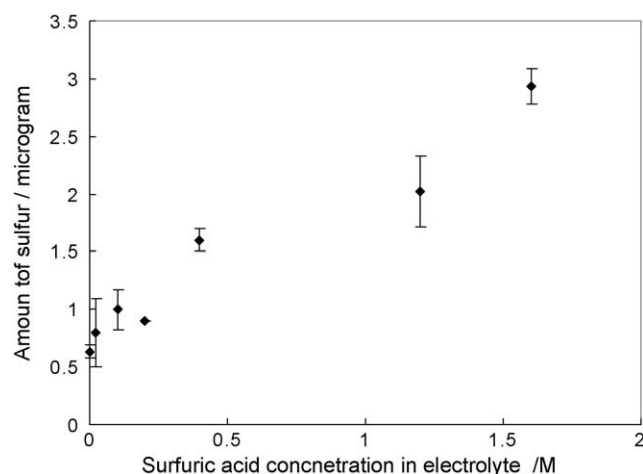


Fig. 7. Plot of the analyzed sulfur content against the sulfuric acid concentration in the electrolyte.

The rutile-structured TiO_2 prepared here exhibits photocatalytic activity under illumination with light of a wavelength longer than the band gap of pristine rutile TiO_2 (413 nm), indicating that the band gap has been narrowed by sulfur doping [16,17]. The site occupation of the sulfur should be able to be determined by structural analysis. Using the rigid sphere model, the possibilities of S^{4+} (0.037 nm) substitution into a Ti^{4+} (0.061 nm) site or S^{2-} (0.184 nm) substitution into an O^{2-} (0.138 nm) site are not plausible. Further studies to determine the sulfur occupation site in the rutile are in progress by neutron diffraction analysis.

4. Conclusions

The photocatalytic activity of rutile-structured TiO_2 prepared by anodic oxidation in a sulfuric acid electrolyte has been investigated. It bleached MB aqueous solution under illumination with light with wavelengths longer than those corresponding to the band gap of monolithic rutile TiO_2 . AES and infrared absorption analyses clarified the presence of sulfur in the anodized oxide. It was concluded that the improved photocatalytic activity under visible light illumination was due to the band gap narrowing by sulfur doping.

Acknowledgments

The authors wish to thank Ms. Y. Matsuda, Mr. S. Sugiyama, Mr. Y. Murakami, Dr. T. Ashino, and Mr. F. Sakamoto from IMR, Tohoku

Univ. and Mr. M. Yamane from Kitami Institute of Technology. The authors are grateful to Asahi Spectra Co., Ltd. for the use of the Xe lamp. One of the authors (N.M.) gratefully acknowledges the Grant-in-Aid for Scientific Research (A) (No. 17206070) from the Ministry of Education, Science, Sports, and Culture, Japan.

References

- [1] A. Fujishima, K. Honda, *Nature* 238 (1972) 37–38.
- [2] N. Negishi, T. Iyoda, K. Hashimoto, A. Fujishima, *Chem. Lett.* 24 (1995) 841–842.
- [3] U. Backman, A. Auvinen, J.K. Jokiniemi, *Surf. Coat. Technol.* 192 (2005) 81–87.
- [4] P.A. Christensen, T.P. Curtis, B. Place, G.M. Walker, *Water Res.* 36 (2002) 2410–2413.
- [5] D. Dumitriu, A.R. Bally, C. Ballif, P. Hones, P.E. Schmid, R. Sanjinés, F. Lévy, V.I. Părvulescu, *Appl. Catal. B* 25 (2000) 83–92.
- [6] (a) K. Shankar, K.C. Tep, G.K. Mor, C.A. Grimes, *J. Phys. D: Appl. Phys.* 39 (2006) 2361–2366;
(b) D. Velten, V. Biehl, F. Aubertin, B. Valeske, W. Possart, J.J. Breme, *Biomed. Res.* 59 (2002) 18–28;
(c) A.G. Mantzila, M.I. Prodromidis, *Electrochim. Acta* 51 (2006) 3537–3542.
- [7] R. Palombari, M. Ranchella, C. Rol, G.V. Sebastiani, *Sol. Energy Mater. Sol. Cells* 71 (2002) 359–368.
- [8] N. Masahashi, S. Semboshi, N. Ohtsu, M. Oku, *Thin Solid Films* 516 (2008) 7488–7496.
- [9] N. Masahashi, Y. Mizukoshi, S. Semboshi, N. Ohtsu, *Appl. Catal. B* 90 (2009) 255–261.
- [10] N. Masahashi, Y. Mizukoshi, S. Semboshi, N. Ohtsu, *Chem. Lett.* 37 (2008) 1126–1127.
- [11] E. Borgarello, J. Kiwi, M. Grätzel, E. Pelizzetti, M. Visca, *J. Am. Chem. Soc.* 104 (1982) 2996–3002.
- [12] W. Choi, A. Termin, M.R. Hoffmann, *J. Phys. Chem.* 98 (1994) 13669–13679.
- [13] V. Brezová, A. Blažková, L. Karpinský, J. Grošková, B. Havlínová, V. Jorík, M. Čepčan, *J. Photochem. Photobiol. A* 15 (1997) 177–183.
- [14] N. Koshida, H. Yabumoto, *Nucl. Instrum. Methods Phys. Res. Sect. B* 59 (1991) 1236–1239.
- [15] M. Anpo, M. Takeuchi, *J. Catal.* 216 (2003) 505–516.
- [16] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science* 293 (2001) 269–271.
- [17] T. Ohno, M. Akiyoshi, T. Umabayashi, K. Asai, T. Mitsui, M. Matsumura, *Appl. Catal. A* 265 (2004) 115–121.
- [18] T. Ohno, T. Mitsui, M. Matsumura, *Chem. Lett.* 32 (2003) 364–365.
- [19] T. Umabayashi, T. Yamaki, H. Itoh, K. Asai, *Appl. Phys. Lett.* 81 (2002) 454–456.
- [20] T. Umabayashi, T. Yamaki, S. Tanaka, K. Asai, *Chem. Lett.* 32 (2003) 330–331.
- [21] T. Umabayashi, T. Yamaki, S. Yamamoto, A. Miyashita, S. Tanaka, T. Sumita, K. Asai, *J. Appl. Phys.* 93 (2003) 5156–5160.
- [22] X. Tang, D. Li, *J. Phys. Chem. C* 112 (2008) 5405–5409.
- [23] X. Chen, P.-A. Glans, X. Qiu, S. Dayal, W.D. Jennings, K.E. Smith, C. Burda, J. Guo, *J. Electron Spectrosc. Relat. Phenom.* 162 (2008) 67–73.
- [24] N. Serpone, *J. Phys. Chem. B* 110 (2006) 24287–24293.
- [25] (a) G.K. Mor, O.K. Varghese, M. Paulose, K. Shankar, C.A. Grimes, *Sol. Energy Mater. Sol. Cells* 90 (2006) 2011–2075;
(b) L. Lei, Y. Su, M. Zhou, X. Zhang, X. Chen, *Mater. Res. Bull.* 42 (2007) 2230–2236.
- [26] I.K. Konstantinou, T.A. Albanis, *Appl. Catal. B* 49 (2004) 1–14.
- [27] T. Zhang, T. Oyama, A. Aoshimaa, H. Hidaka, J. Zhao, N. Serpone, *J. Photochem. Photobiol. A* 140 (2001) 163–172.
- [28] D.I. Sayago, P. Serrano, O. Böhme, A. Goldoni, G. Paolucci, E. Román, J.A. Martín-Gago, *Phys. Rev. B* 64 (2001) 205402–205407.
- [29] C.A. Muryn, P.J. Hardman, J.J. Crouch, G.N. Raiker, G. Thornton, D.S.L. Law, *Surf. Sci.* 251–252 (1991) 747–752.
- [30] L.-Q. Wang, D.R. Baer, M.H. Engelhard, A.N. Shultz, *Surf. Sci.* 344 (1995) 237–250.